Journal Name

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Aluminium salalen complexes based on 1,2-diaminocyclohexane and their exploitation for the polymerisation of *rac*-lactide

Stuart L. Hancock, Mary F. Mahon and Matthew D. Jones*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

In this paper nine various salalen ligands have been prepared and characterised. The steric and electronic effects of both the salen and salan fragments have been varied in a systematic fashion to ascertain how this affects the selectivity for the ROP of *rac*-lactide. These were complexed to $AlMe_3$ to generate pseudo trigonal bypyramidal metal centred complexes. Upon addition of benzyl alcohol the active initiator can be easily prepared. The complexes were screened for the ROP of *rac*-lactide in solution and melt conditions. PLA with narrow molecular weight distributions (PDIs range from 1.07 – 1.67) could be isolated with moderate degrees of tacticity. Significantly it was found that chloro groups on the imine fragment increased the degree of heterotactic enchainment in the polymer. The kinetics for one series of salalen-Al complexes was also investigated.

Introduction

In recent years the metal catalysed polymerisation of lactide to produce polylactide (PLA) has been a "hot-topic" and will continue to be so for more years to come.[1] This is due to the favourable properties of the polymer – namely biodegradability and the fact that it can be sourced from renewable materials. Lactide can be prepared from lactic acid which in-turn is produced from fermentation of starch.[2] PLA has found utility in markets such as high value medical devices to more traditional commodity based applications.[3] Furthermore, if the racemic version of the monomer is used (*rac*-lactide or *rac*-LA) then various stereoforms of PLA can be prepared (heterotactic, atactic and stereoblock isotactic).[4] Many metal centres have been employed in the production of PLA – for example groups 1-4,[5] lanthanides,[6] Zn(II)[7] and Sn(II).[8] One of the main Lewis acid metals centres that is suitable for this polymerisation is Al(III). Pioneering work by Feijen,[9] Chisholm,[10] Nomura[11] and Gibson[12] (amongst others) have shown that initiators based on Al(III) can produce controlled molecular weight PLA and are capable of inducing stereoselectivity into the final polymer.[12] Without question the two main ligands bound to the aluminium centres are based on salan or salen moieties.[9-12] These are typically symmetrical in nature – due to their preparation.

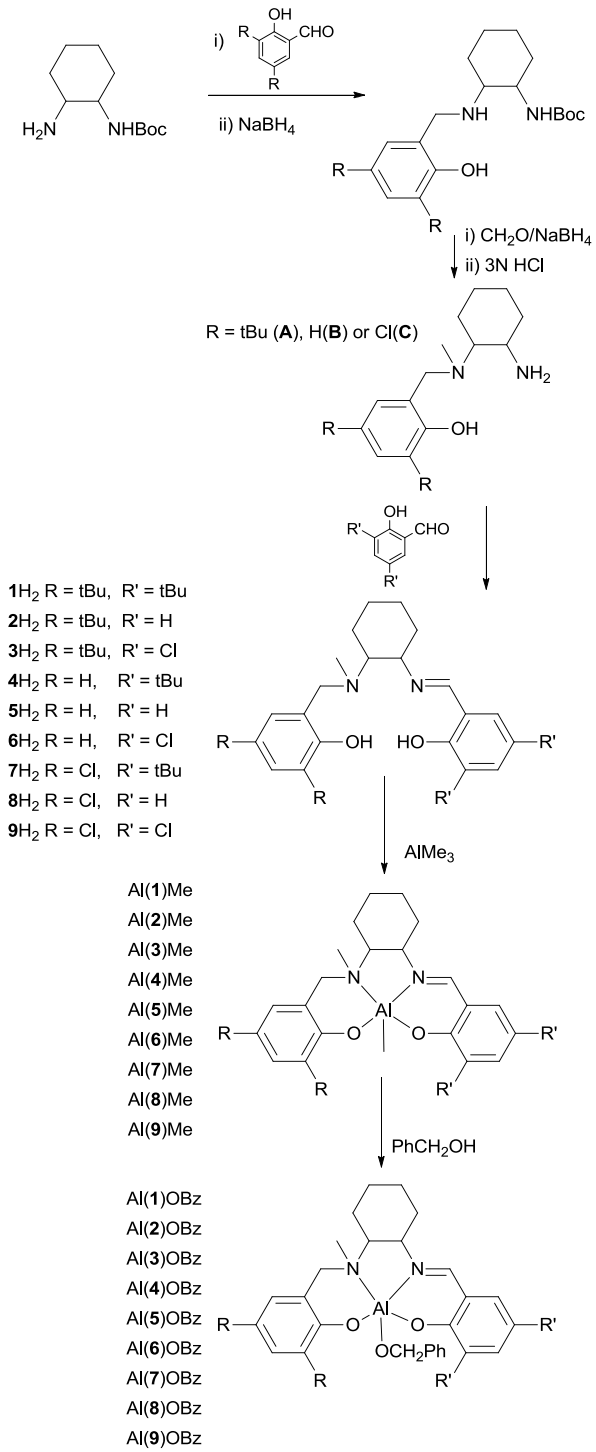
Recently, Katsuki and co-workers have prepared a series of salalen complexes for the enantioselective hydrophosphonylation of aldehydes and aldimines; and sulphur oxidations.[13] High enantioselectivies and conversions have been reported. An advantage of such systems is there is a high degree of synthetic variation possible in terms of the sterics/electronics of either phenyl ring. Kol and co-workers have recently shown that Ti(IV) salalen complexes are active for the isospecific polymerisation of 1-hexene and propylene.[14] We have previously reported the utility of group 4 salalen complexes for the polymerisation of *rac*-lactide.[15] Furthermore, we have recently shown that Al(III)-salalen complexes can produce either isotactic or heterotactic PLA depending on the nature of the substituent on the amine nitrogen centre.[16] One of the foremost Al(III) complexes prepared to date was based on Jabobsen's ligand[17] {(*R*,*R*)-(-)-N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-diaminocyclohexane} with highly isotactic PLA being produced.[9] In this paper we have prepared a range of salalen ligands based on the 1,2-diaminocyclohexane backbone, complexed these to Al(III) and tested for the ring opening polymerisation of *rac*-lactide in solution and under the industrially preferred melt conditions.

Results and Discussion

Ligand and Complex Preparation

The ligands were prepared by modified literature procedures, as shown in scheme 1.[13d] The *trans* form (*R*,*R* or *S*,*S*) of 1,2-diaminocyclohexane was initially mono-protected and treated with an equivalent of an aldehyde and subsequent reduction generated an amine. Addition of formaldehyde and $NaBH_4$ generated the N-Me moiety, subsequent deprotection formed an amine. This was treated with another equivalent of aldehyde to form the salalen ligand. Depending on aldehyde utilised a whole host of various ligands could be prepared in high purity and good yields. The *R*,*R* chiral form of the diamine was utilised to prepare the enantiopure form of ligand **1**H_2. All ligands were characterised by $^1H/^{13}C\{^1H\}$NMR spectroscopy and HR-MS. The salalen ligands **1**H_2-**9**H_2 were treated with an equivalent of $AlMe_3$ to generate Al(**1**-**9**)Me subsequent addition of benzyl alcohol generated Al(**1**-**9**)OCH_2Ph. The Al-Me complexes containing salalen ligands without the presence of *t*Bu (**5**H_2, **6**H_2, **8**H_2, **9**H_2) moieties were not soluble in common organic solvents, but could

be reacted with benzyl alcohol to generate the alkoxide species.



Scheme 1 Ligands and Complexes prepared in the study

Complexes Al(**1**)Me, Al(*R*,*R*-**1**)Me and Al(**4**)OCH_2Ph have been characterised by single crystal X-ray diffraction. See Figure 1 for solid-state structures of Al(**1**)Me and Al(**4**)OCH_2Ph and Table 1 for selected bond distances and angles. When the ligands are complexed there are three stereocentres in the complexes – with the carbon centres in the diaminocyclohexane ring being locked in either the *R*,*R* or *S*,*S* (for the racemic form of the *trans*-ligand) and when complexed the amine nitrogen centre also becomes chiral. We have also prepared the stereopure version of **1**H_2 (*R*,*R*-**1**H_2) as a structural comparison. As expected the Al-N_{imine} is significantly shorter than the Al-N_{amine}. The metal centres are in pseudo trigonal bypyramidal geometries as expected for such complexes.[18] This is exemplified by the N(1)-Al(1)-O(2) angle of *ca*. 170 º and O(1)-Al(1)-N(2) of *ca*. 120 º. Complexes containing Al-OCH_2Ph are rare compared to their Al-Me counterparts.[11b, 18]

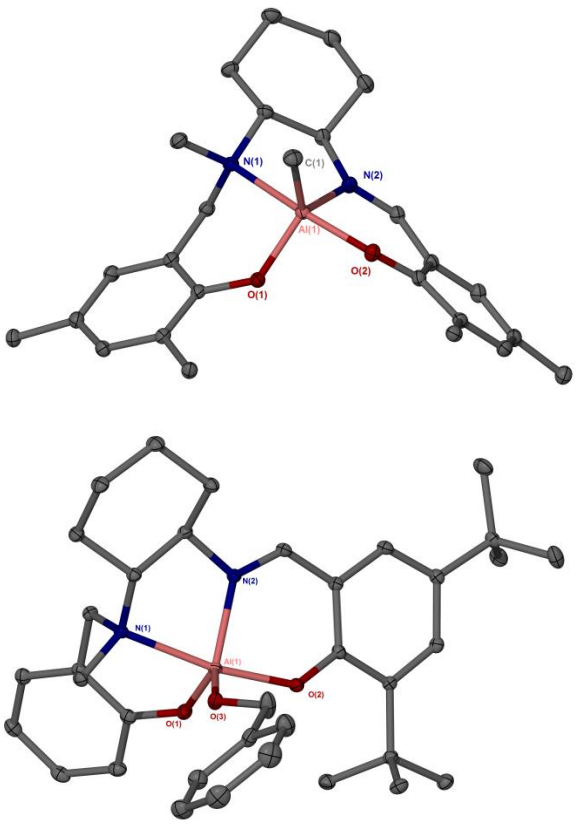


Fig.1 Solid state structure for Al(**1**)Me (top, the Me groups of the *t*Bu moieties have been removed for clarity) and Al(**4**)OCH_2Ph (bottom). The ellipsoids are shown at the 30% probability level and all hydrogen atoms have been removed for clarity.

Table 1 Selected bond lengths (Å) and angles (º) for the complexes isolated in the solid-state.

	Al(**1**)Me	Al(*R*,*R*-**1**)Me	Al(**4**)OCH_2Ph
Al(1)-O(1)	1.769(4)	1.7665(15)	1.7714(11)
Al(1)-O(2)	1.834(4)	1.8339(13)	1.8065(10)
Al(1)-N (1)	2.178(5)	2.2083(16)	2.1192(12)
Al(1)-N(2)	1.980(5)	1.9801(17)	1.9652(12)
Al(1)-C(1)	1.968(6)	1.968(2)	-
Al(1)-O(3)		-	1.7335(11)
O(1)-Al(1)-O(2)	93.0(2)	94.43(6)	90.68(5)
O(1)-Al(1)-N(1))	88.87(19)	87.73(6)	88.71(5)
O(1)-Al(1)-N(2)	117.8(2)	117.78(7)	124.07(5)
N(1)-Al(1)-O(2)	164.4(2)	165.72(6)	167.62(5)

With Al(**1**)Me the solid-state structure is indicative of the stereoform where the carbon centres are *R*,*R* and the amine nitrogen has *S* chirality. The space group is $P2_1/n$ thus the enantiomer *S*,*S*,*R* is also present. In the solution-state ^{1}H NMR

spectrum for this complex there is only one Al-Me resonance at -0.35 ppm and one resonance for the N-Me group. For Al(*R*,*R*-**1**)Me the solid structure indicates that the chiral centre on the amine has the *R* configuration, in this case we have utilised the enantiopure ligand. However, dependent upon recrystallisation strategy two isomers were present in solution – presumably originating from the stereoforms in-which the amine chiral centre was either *R* or *S* and the carbon centres fixed. The exact stereoisomer isolated is highly sensitive to recrystallisation procedure, for example we have NMR spectroscopic evidence for either the *R*,*R*,*R*/*S*,*S*,*S* enantiomer pairings being solely formed or the *R*,*R*,*R*/*S*,*S*,*S* *R*,*R*,*S*/*S*,*S*,*R* diastereomers being formed with the same ligands (full characterisation details are given in the supporting information).† Upon heating (80 ºC in $C_6D_5CD_3$) in solution both sets of diastereomers are observed, regardless of the isolation procedure. Thus, indicating the same ratio of complexes are initiating the polymerisation of lactide. For the alkoxide complexes, again, the exact stereoisomer formed was highly dependent upon recrystallisation conditions and showed the same trend as the Al-Me complexes upon heating.

Polymerisation Study

Initially the polymerisations were run under melt conditions, Table 2. Complexes containing *t*Bu moieties gave relatively low conversions, whereas those with ortho H substituents gave significantly higher conversions. This is presumably a steric effect due to hindered attack of the lactide at the metal centre. Al(**1**)OBn produced PLA with a very slight heterotactic bias, this is in stark contrast to the analogous double salen ligand complex of Feijen which is one of the most effective initiators for the production of isotactic PLA from *rac*-LA under melt conditions. The difference in stereoselectivity is conceivably an effect of the enhanced flexibility about the amine bond. Also noteworthy is that complexes with a chloro group on the imine fragment of the salalen produce PLA with a heterotactic bias.

Table 2 Melt polymerisation data.

Melt	Time (h)	Conv. (%)[a]	M_n[b]	PDI[b]	P_r[c]
Al(**1**)OBn	48	30	7850	1.07	0.54
Al(**2**)OBn	24	85	57600	1.51	0.58
Al(**3**)OBn	24	91	48150	1.71	0.64
Al(**4**)OBn	24	27	9100	1.06	0.41
Al(**5**)OBn	2	42	28700	1.07	0.51
Al(**6**)OBn	2	94	33350	1.10	0.57
Al(**7**)OBn	24	68	14300	1.56	0.43
Al(**8**)OBn	2	98	46550	1.47	0.61
Al(**9**)OBn	24	60	23350	1.14	0.72

Conditions: Monomer:initiator ratio 300:1, T = 130 °C. [a] determined from ^{1}H NMR analysis; [b] determined from GPC analysis using THF as the solvent and reference to polystyrene standards; [c] determined from the analysis of the methine region of the ^{1}H homonuclear decoupled NMR spectrum.

The solution polymerisation data is shown in Table 3. Either the Al-OCH_2Ph or Al-Me (with the addition of 1 eq. of $PhCH_2OH$ in-situ) were utilised as the initiators. The polymerisation yielded PLA with relatively controlled M_n values and low PDIs {with the exception of Al(**8**)OBn}. Interestingly, for complexes containing ligands **4**H_2 and **7**H_2 the alkoxide complexes gave a significantly lower conversion than the alkoxide generated from the Al-Me complex. In agreement with Feijen's Al(III) initiator employing Jacobsen's ligand the polymerisation was relatively slow requiring several days to achieve significant conversion. The kinetics have been investigated with ligands **4**H_2-**6**H_2 (H substituents on the amine half) to ascertain the effect of changing the substituent on the imine, Figure 2. The chloro substituted ligand being significantly faster than the H-substituted ligand which in-turn is faster than the *t*Bu ligand. The former trend is presumably an electronic effect whereas the latter is related to steric hindrance around the metal centre.

Table 3 Solution polymerisation data.

	Time (days)	Conv. (%)[a]	M_n[b]	PDI[b]	P_r[c]
Al(**1**)Me	4	34	-[d]	-[d]	0.49
Al(**1**)OBn	4	26	3750	1.08	0.54
Al(**2**)Me	4	71	12200	1.07	0.65
Al(**2**)OBn	4	91	19550	1.12	0.61
Al(**3**)Me	4	97	17150	1.35	0.60
Al(**3**)OBn	4	99	17000	1.18	0.69
Al(**4**)Me	4	83	7700	1.06	0.57
Al(**4**)OBn	10	40	6400	1.08	0.42
Al(**5**)OBn	4	96	24600	1.12	0.56
Al(**6**)OBn	4	96	19900	1.27	0.54
Al(**7**)Me	4	61	7100	1.07	0.54
Al(**7**)OBn	10	49	8300	1.06	0.31
Al(**8**)OBn	4	96	14600	1.67	0.54
Al(**9**)OBn	4	99	19350	1.15	0.73

Conditions: Monomer:initiator ratio 100:1(:1BnOH if required) solvent toluene, T = 80 °C. [a] determined from ^{1}H NMR analysis; [b] determined from GPC analysis using THF as the solvent and reference to polystyrene standards; [c] determined from the analysis of the methine region of the ^{1}H homonuclear decoupled NMR spectrum. [d] M_n could not be determined.

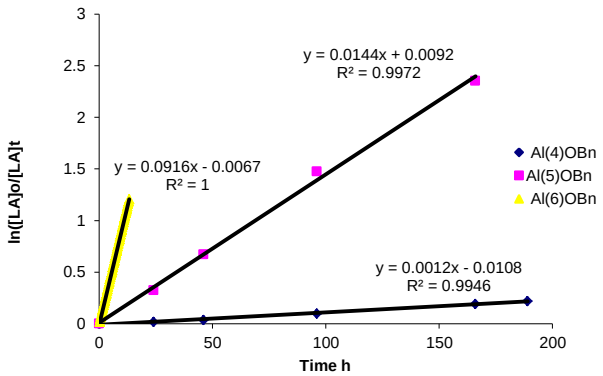


Fig 2 Kinetic measurements for the solution polymerisation of *rac*-LA with Al(**4**-**6**)OBn at 80 °C with a [LA]:[Init] ratio 100:1 in d_8-tol ($[LA]_0$ = 0.578 moldm^{-3}).

Conclusions

In conclusion a series of Al(III) salalen complexes have been prepared and structurally characterised. These complexes have been tested for the ROP of *rac*-LA. The steric and electronic influences of the substituents on both the salen and salan fragments of the ligand have been investigated and are discussed. Chloro groups on the imine side tend to induce heterotactic enchainment.

Acknowledgments

We would like to thank the University of Bath and the EPRSC (DTA) for funding a studentship for SLH.

Experimental

For the preparation and characterisation of metal complexes, all reactions and manipulations were performed under an inert atmosphere of argon using standard Schlenk or glovebox techniques. *rac*-LA (Aldrich) was recrystallised from toluene and sublimed twice prior to use. All other chemicals were purchased from Aldrich. All solvents used in the preparation of metal complexes and polymerisation reactions were dry and obtained *via* SPS (solvent purification system). ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker 250, 300 or 400 MHz instrument and referenced to residual solvent peaks. Coupling constants are given in Hertz. Elemental analyses were performed by Mr Stephen Boyer, London Metropolitan University. The ligands were prepared according to standard literature procedures and the purity confirmed *via* ^{1}H/^{13}C{^{1}H} NMR spectroscopy and HR-MS prior to use.

Ligand and Complex Preparation

Typical procedures are as follows, see supporting information for the characterisation of other ligands and their complexes.

A *tert*-Butyl (2-aminocyclohexyl)carbamate (2.00 g, 9.33 mmol) was added to a solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (2.18 g, 9.30 mmol) in MeOH (30 ml) / THF (30 ml) and stirred for 1 h. $NaBH_4$ (2.12 g, 56.03 mmol) was added slowly to the yellow solution and then stirred for 5 h until the solution became colourless. The reaction was quenched with water (10 ml) and the solvent partially removed *in-vacuo*. Water (50 ml) was then used to precipitate a white solid, which was then filtered and washed with water (3 × 50 ml). The resulting solid was dissolved in MeOH (30 ml) and formaldehyde solution (37 % in H_2O, 2.12 ml, 26.74 mmol) was slowly added and allowed to stir for 1 h. The solvent was removed *in-vacuo* and the residue was dissolved in MeOH (30 ml) / THF (30 ml) and cooled (0 °C), then $NaBH_4$ (2.12 g, 56.03 mmol) was slowly added and the solution was stirred for 2 h. The reaction was quenched with water (10 ml) and the solvent partially removed *in-vacuo*. Water (50 ml) was then used to precipitate a white solid, which was then filtered and washed with water (3 × 50 ml) and dried to yield a white solid (3.40 g, 7.61 mmol, 82 %). ^{1}H NMR ($CDCl_3$): δ 1.00 – 1.20 (2H, m, CH_2), 1.28 (9H, s, ^{t}Bu), 1.43 (9H, s, ^{t}Bu), 1.48 (9H, s, ^{t}Bu), 1.60 – 2.10 (6H, m, CH_2), 2.29 (3H, s, CH_3), 2.36 (1H, m, CH), 3.62 (1H, m, CH), 3.75 (1H, m, NH), 3.79 (1H, d, J = 4.5 Hz, CH_2), 4.55 (1H, d, J = 10.0 Hz, CH_2), 6.81 (1H, d, J = 2.5 Hz, ArH), 7.21 (1H, d, J = 2.5 Hz, ArH), 11.10 (1H, br, ArOH). Deprotection: (2.40 g, 5.37 mmol) was dissolved in methanol (30 ml) and 3M HCl (30 ml) then heated to 60 °C and allowed to stir (16 h). The mixture was neutralised with 3M NaOH and the white precipitate was extracted with AcOEt (4 × 20 ml). The organic phase was washed with saturated brine (20 ml) then dried with $MgSO_4$, the solid was removed by filtration and the solvent removed *in-vacuo* to yield an oily residue which was used without further purification (1.80 g, 5.19 mmol, 97 %). ^{1}H NMR ($CDCl_3$): δ 1.10 – 1.3 (4H, m, CH_2), 1.28 (9H, s, CH_3), 1.41 (9H, s, CH_3), 1.65 - 2.05 (4H, m, CH_2), 2.25 (3H, s, CH_3), 2.35 (1H, m, CH), 2.79 (1H, m, CH), 3.72 (1H, d, J = 13.5 Hz, CH_2), 3.86 (1H, d, J = 13.5 Hz, CH_2), 4.12 (1H, q, J = 7.5 Hz, NH) 3.50 – 4.00 (3H, br, NH_2, ArOH), 6.83 (1H, d, J = 2.5 Hz, ArH), 7.21 (1H, d, J = 2.5 Hz, ArH).

2H_2. **A** (1.00 g, 2.89 mmol) was dissolved in MeOH (30 ml) and 2-hydroxybenzaldehyde (0.31 ml, 2.91 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried *in-vacuo* to yield a yellow solid (0.98 g, 2.17 mmol, 75 %). ^{1}H NMR ($CDCl_3$): δ 1.11 (9H, s, ^{t}Bu), 1.25 (9H, s, ^{t}Bu), 1.31 – 1.53 (3H, m, ring-CH_2), 1.63 – 2.08 (5H, m, ring-CH_2), 2.20 (3H, s, CH_3), 2.97 (1H, m, ring-CH), 3.36 (1H, m, ring-CH), 3.70 (1H, br, CH_2), 3.80 (1H, d, J = 13.0 Hz, CH_2), 6.77 (1H, d, J = 2.0 Hz, ArH), 6.86 (1H, t, J = 7.5 Hz, ArH), 6.99 (1H, d, J = 8.0 Hz, ArH), 7.11 (1H, br, ArH), 7.23 (1H, d, J = 7.5 Hz, ArH), 7.42(1H, td, J = 8.0 Hz, , J = 2.0 Hz, ArH), 8.38 (1H, s, CH), 10.62 (1H, br, OH), 13.15 (1H, s, OH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.1 (CH_2), 24.6 (CH_2), 25.1 (CH_2), 29.3 (CH_3), 31.7 (CH_3), 34.1 (C), 34.6 (C), 34.9 (CH_2), 58.5 (CH_2), 67.2 (CH), 70.1 (CH), 117.0 (ArH), 118.4 (ArH), 119.1 (Ar), 120.7 (Ar), 122.5 (ArH), 123.1 (ArH), 131.3 (ArH), 132.1 (ArH), 135.4 (Ar), 139.8 (Ar), 154.6 (Ar-O), 161.2 (Ar-O), 164.7 (N=CH). Calc. m/z $[C_{29}H_{42}N_2O_2 + Na]^+$ 473.3144. Found 473.3166

Al(**2**)Me. **2**H_2 (0.45 g, 1.00 mmol) was dissolved in toluene (30 ml) then 2M $AlMe_3$ in heptane (0.50 ml, 1.00 mmol) was slowly added and stirred (16 h). The solvent was removed *in-vacuo* and the crude mixture was recrystallised from toluene to yield yellow crystals (0.10 g, 0.20 mmol, 20 %). ^{1}H NMR (d_8-Tol): δ -0.36 (3H, s, Al-Me), 0.70 - 1.00 (4H, br, ring-CH_2), 1.30 – 1.60 (4H, m, ring-CH_2), 1.45 (9H, s, ^{t}Bu), 1.75 (9H, s, ^{t}Bu), 1.86 (3H, s, CH_3), 2.45 – 2.65 (2H, m, ring-CH), 2.72 (1H, d, J = 12.0 Hz, CH_2), 3.49 (1H, d, J = 12.0 Hz, CH_2), 6.53 (1H, ddd, J = 8.0 Hz, J = 6.5 Hz, J = 1.5 Hz, ArH), 6.90 (1H, d, J = 1.5 Hz, ArH), 6.93 (1H, d, J = 2.0 Hz, ArH), 7.14 (1H, d, J = 1.5 Hz, ArH), 7.18 (1H, dd, J = 6.5 Hz, J = 2.0 Hz, ArH), 7.52 (1H, d, J = 2.5 Hz, ArH), 7.69 (1H, s, CH). ^{13}C{^{1}H} NMR (d_8-Tol): δ 29.7 (CH_2), 29.8 (CH_2), 34.8 (CH_3), 37.1 (CH_3), 38.0 (C), 39.1 (C), 40.3 (CH_2), 45.5 (CH_3), 57.2 (CH_2), 66.7 (CH), 70.9 (CH), 120.1 (ArH), 123.4 (Ar), 126.4 (Ar), 127.8 (ArH), 128.3 (ArH), 128.6 (ArH), 138.7 (ArH), 142.1 (ArH), 142.7 (Ar), 143.3 (Ar), 162.1 (Ar-O), 173.9 (Ar-O), 176.3 (N=CH). Calc.(%) for $C_{30}H_{43}AlN_2O_2$; C 73.44, H 8.83, N 5.71. Found (%); C 73.57, H 8.83, N 5.80.

Al(**2**)OBn. **2**H_2 (0.36 g, 0.80 mmol) was dissolved in toluene (30 ml) then 2M $AlMe_3$ in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed *in-vacuo*, then the residue was dissolved in toluene (30 ml). Benzyl alcohol (0.083 ml, 0.80 mmol) was slowly added to the reaction and allowed to stir (16 h). The solvent was removed *in-vacuo* and the crude mixture was recrystallised from hexane to yield a yellow solid (0.06 g, 0.09 mmol, 11 %). ^{1}H NMR (d_8-Tol) (233 K): δ 0.40 – 0.65 (4H, m, ring-CH_2), 1.05 – 1.30 (4H, m, ring-CH_2), 1.46 (9H, s, ^{t}Bu), 1.74 (9H, s, ^{t}Bu), 2.21 (3H, s, CH_3), 2.29 (2H, br, ring-CH), 2.88

(1H, d, J = 13.5 Hz, CH_2), 4.56 (1H, d, J = 13.5 Hz, CH_2), 5.31 (1H, d, J = 14.0 Hz, CH_2), 5.57 (1H, d, J = 14.0 Hz, CH_2), 6.56 (1H, t, J = 7.5 Hz, ArH), 6.82 (1H, s, ArH), 6.87 (1H, d, J = 7.5 Hz, ArH), 7.04 (1H, s, ArH), 7.20 (1H, s, ArH), 7.23 (1H, s, ArH), 7.29 (2H, t, J = 7.5 Hz, ArH), 7.41 (1H, s, ArH), 7.56 (1H, s, ArH), 7.60 (1H, s, ArH), 7.62 (1H, s, OH). $^{13}C\{^1H\}$ NMR (d_8-Tol): δ 25.0 (CH_2), 25.6 (CH_2), 30.9 (CH_3), 32.7 (C), 33.2 (CH_3), 36.4 (C), 38.6 (CH_3), 60.3 (CH_2), 60.7 (CH), 60.9 (CH), 67.5 (CH_2), 116.9 (ArH), 118.9 (Ar), 121.3 (Ar), 122.0 (Ar), 123.1 (ArH), 124.0 (ArH), 126.0 (ArH), 126.2 (ArH), 127.3 (ArH), 128.4 (ArH), 129.7 (ArH), 134.2 (ArH), 137.5 (ArH), 138.7 (Ar), 138.8 (Ar), 143.3 (Ar), 157.2 (Ar-O), 168.1 (Ar-O), 170.6 (N=CH). Calc.(%) for $C_{36}H_{47}AlN_2O_3$; C 73.20, H 8.13, N 4.81. Found (%); C 72.31, H 7.86, N 4.47.

Polymerisation

For solvent-free polymerisations the monomer:initiator ratio employed was 300:1 at a temperature of 130 °C, in all cases 1.0 g of *rac*-lactide was used. After the reaction time methanol (20 ml) was added to quench the reaction and the resulting solid was dissolved in dichloromethane. The solvents were removed in-vacuo and the resulting solid washed with methanol (3 × 50 ml) to remove any unreacted monomer. For solution polymerisations a monomer:initiator ratio of 100:1(:1 if benzyl alcohol was necessary) was used. In all cases 1.0 g of lactide and the appropriate amount of initiator were dissolved in toluene (10 ml) these were placed in a pre-heated oil bath and heated for the desired amount of time. The reaction was quenched by the addition of methanol (20 ml). ^1H NMR spectroscopy ($CDCl_3$) and GPC (THF) were used to determine tacticity and molecular weights (M_n and M_w) of the polymers produced; $P_{r/m}$ (the probability of heterotactic/isotactic linkages) were determined by analysis of the methine region of the homonuclear decoupled ^1H NMR spectra.[19] Gel Permeation Chromatography (GPC) analyses were performed on a Polymer Laboratories PL-GPC 50 integrated system using a PLgel 5 µm MIXED-D 300 × 7.5 mm column at 35 °C, THF solvent (flow rate 1.0 ml/min). The polydispersity index (PDI) was determined from M_w/M_n where M_n is the number average molecular weight and M_w the weight average molecular weight. The polymers were referenced to polystyrene standards.

Single Crystal Diffraction

All data were collected on a Nonius kappa CCD diffractometer with MoKα radiation, λ = 0.71073 Å, see Table 4. T = 150(2) K throughout and all structures were solved by direct methods and refined on F^2 data using the SHELXL-97 suite of programs.[20] Hydrogen atoms, were included in idealised positions and refined using the riding model. Refinements were generally straightforward with the following exceptions and points of note. Al(**1**)Me R_{int} is higher than desirable and remained so despite extensive recrystallisation efforts, however, the structure has been unambiguously determined. Al(*R*,*R*- **1**)Me contains a molecule of hexane in the asymmetric unit. The asymmetric unit of Al(**4**)OCH_2Ph contains half a molecule of toluene located on an inversion centre.

Table 4 X-ray crystallographic parameters

	Al(*R*,*R*-**1**)Me	Al(**1**)Me	Al(**4**)OCH_2Ph
Chemical formula	$C_{44}H_{73}AlN_2O_2$	$C_{38}H_{59}AlN_2O_2$	$C_{39\cdot50}H_{51}AlN_2O_3$
Formula Mass	689.02	602.85	628.80
Crystal system	Monoclinic	Monoclinic	Monoclinic
a/Å	14.159(2)	11.8730(6)	25.7960(3)
b/Å	10.235(4)	10.6560(7)	12.5570(1)
c/Å	14.801(2)	28.8840(18)	21.7940(2)
α/°	90	90	90
β/°	92.574(7)	94.668(5)	100.521(1)
γ/°	90	90	90
Unit cell volume/Å^3	2142.8(10)	3642.2(4)	6940.84(12)
Space group	$P2_1$	$P2_1/n$	$C2/c$
No. of reflections measured	38513	20442	55806
Flack parameter	-0.01(13)	-	-
No. of independent reflections	9665	6315	7910
R_{int}	0.0612	0.1590	0.0619
Final R_1 values ($I > 2\sigma(I)$)	0.0457	0.1147	0.0422
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0993	0.2056	0.0903
Final R_1 values (all data)	0.0691	0.2204	0.0634
Final $wR(F^2)$ values (all data)	0.1097	0.2450	0.1006

Notes and references

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK. Fax: +44 (0) 1225 386231 Tel: +44 (0) 1225 384908; E-mail: mj205@bath.ac.uk

† Electronic Supplementary Information (ESI) available: [full experimental details and the crystal data in the .cif format]. See DOI: 10.1039/b000000x/

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